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Practical Implications of Closing Up Fiberlines

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Practical Implications of Closing Up Fiberlines

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ABSTRACT

Nonprocess element (NPE) concentrations within the fiberline increase as the degree of fiberline closure increases. Increased concentrations of potassium and chloride can result in recovery boiler fouling. Increased concentrations of calcium and barium can lead to scale deposits on process equipment. Increased concentrations of manganese and iron catalyze the decomposition of hydrogen peroxide leading to reduced bleaching efficiency and/or pulp strength loss in oxygen, ozone, and hydrogen peroxide stages. Closure of the bleach plant water circuits requires controlled purges to manage metals within the fiberline.

INTRODUCTION

Prior to the late 1980s, the first stage of kraft pulp bleaching was based on elemental chlorine and operated below a pH of 2.0. The washer filtrates of the conventional chlorine-based bleach plant were often reused in a counter-current fashion within the bleach plant to reduce energy consumption. However, bleach plant filtrates were not recycled to the brownstock fiberline because of their high chloride content. Bleach plant filtrates were sewered and sent to the effluent treatment system prior to being discharged from the mill. The washer filtrate from the low pH chlorine stage served as an excellent purge of nonprocess elements from the fiberline.

The industry has moved away from elemental chlorine bleaching to chlorine dioxide and oxygen-based bleaching to lower the environmental impact of pulp bleaching. Increased closure of bleach plant filtrates has been possible with this change in bleaching technology, as reported by Union Camp with its high consistency ozone bleaching system(1) and by Champion International with its chlorine dioxide based BFR bleaching system(2). These changes in bleaching technology require proactive management of metals in the fiberline to replace the passive management provided by the environmentally obsolete elemental chlorine bleach stage.

Typical bleached kraft mill fiberline metal profiles for Ca, Mg, Mn, and Fe are shown in Figures 1-4. Bars represent the data range of 10 independent samples collected over a two day period. The process flow diagram for the mill is given in Figure 5. The wood furnish to the mill was primarily Douglas fir, and the C-stage was operating with 50% chlorine dioxide substitution. Complete sampling details and data are given in Ref. (3).

FIBERLINE WASHER EFFICIENCY

Good washing is critical in the modern fiberline to ensure efficient bleaching, minimum discharge of COD to the environment, and removal of transition metals prior to oxidative bleach stages. However, increased washing efficiency increases recovery of the alkali-soluble elements including potassium and chloride.

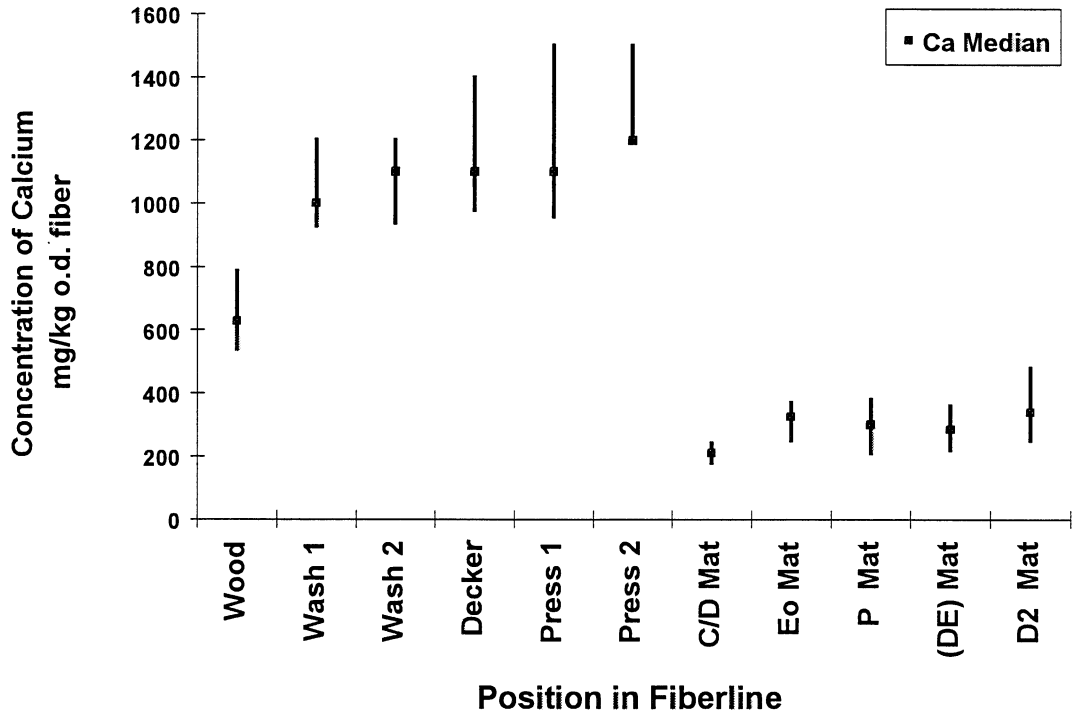

Figure 1. Mill calcium profile.

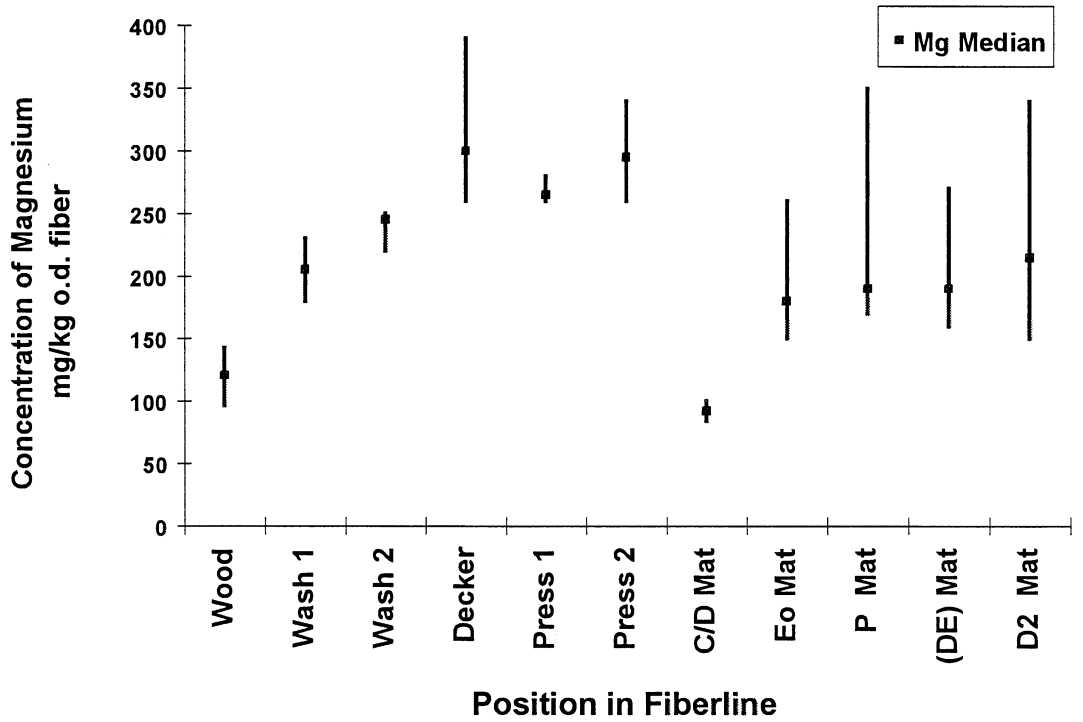

Figure 2. Mill magnesium profile.

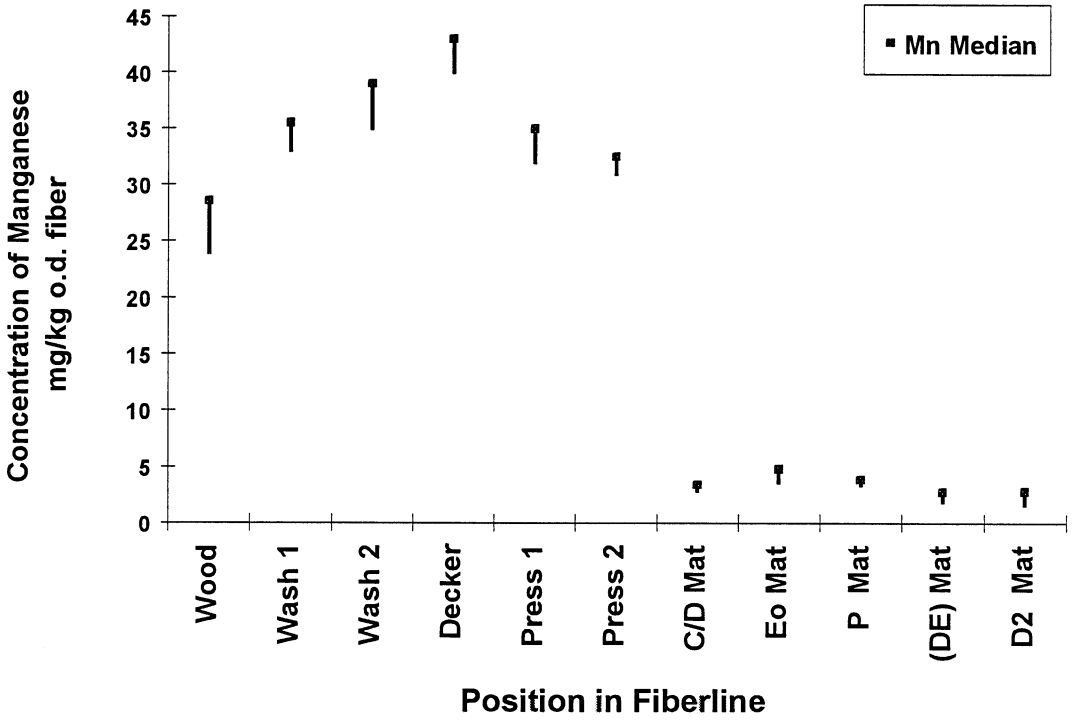

Figure 3. Mill manganese profile.

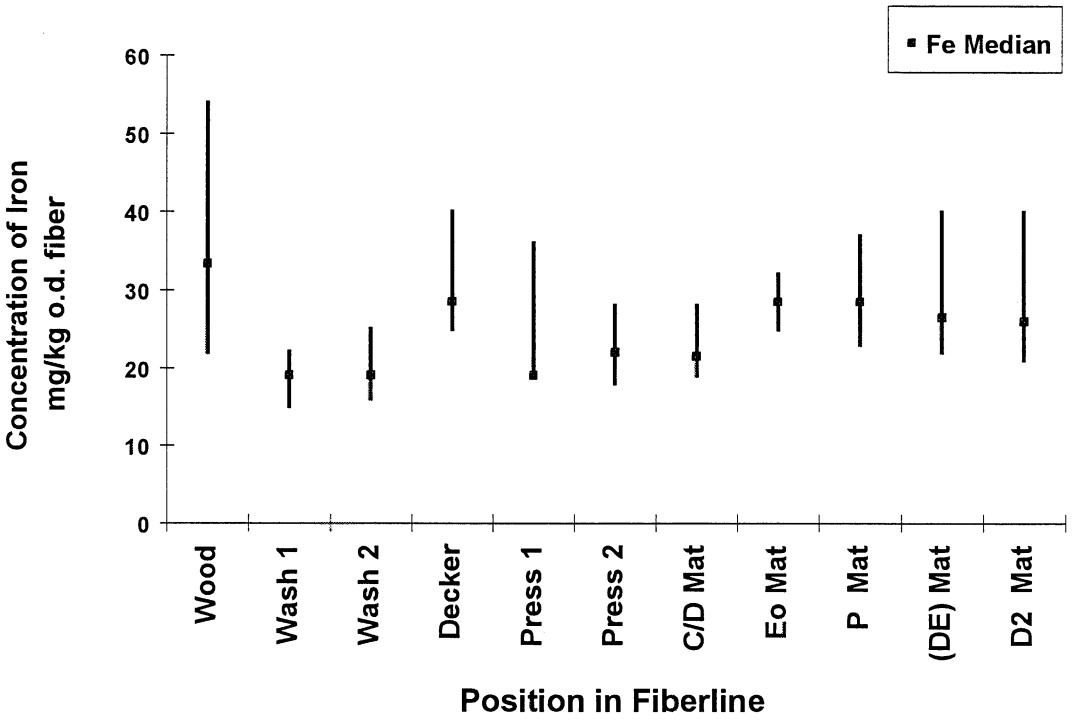

Figure 4. Mill iron profile.

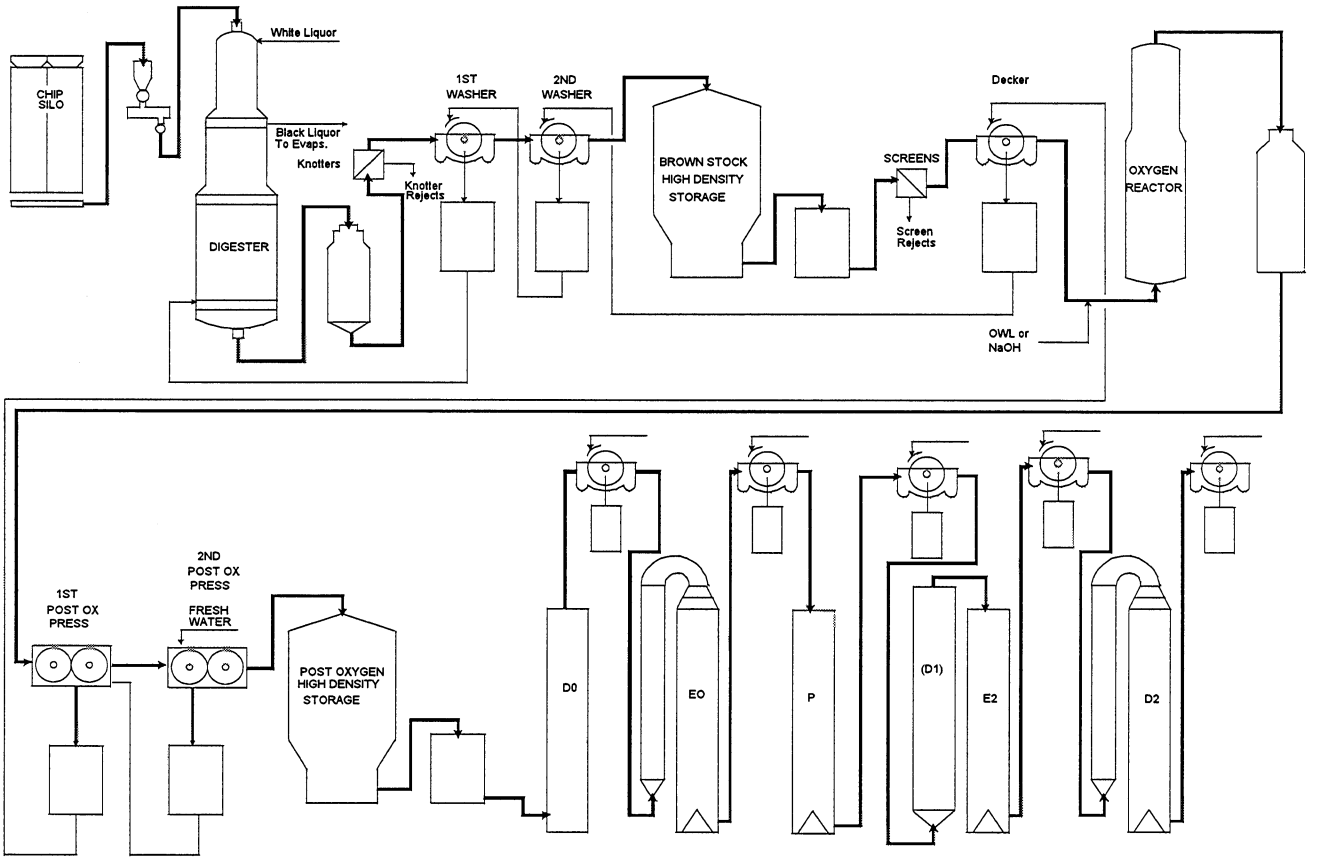

Figure 5. Mill process flow diagram for metal profiles given in Figures 1-4.

Increased chloride and potassium concentrations in the kraft liquor cycle can result in accelerated corrosion, boiler plugging, and ring formation in the lime kiln. Boiler plugging is a concern of many mills because of the production loss incurred when the recovery boiler is shut down for a water wash.

Most of the chloride and potassium entering the liquor cycle comes in the with wood and with the makeup chemicals. There are no intentional purges for alkali-soluble elements in a typical kraft mill operation. Most of the alkali-soluble ions leave the liquor cycle with the pulp off the last brownstock washer and with liquor spills or other unintentional pulp and liquor losses. A small portion of chloride and potassium is purged with the tall oil, boiler flue gas, grits, dregs, lime, etc.

One of the economic advantages of the kraft process is a high level of cooking chemical recovery. To illustrate the effect of recycle (or recovery) on trace contaminate buildup, the material balance of a simple single-recycle-loop process is shown in Figure 6.

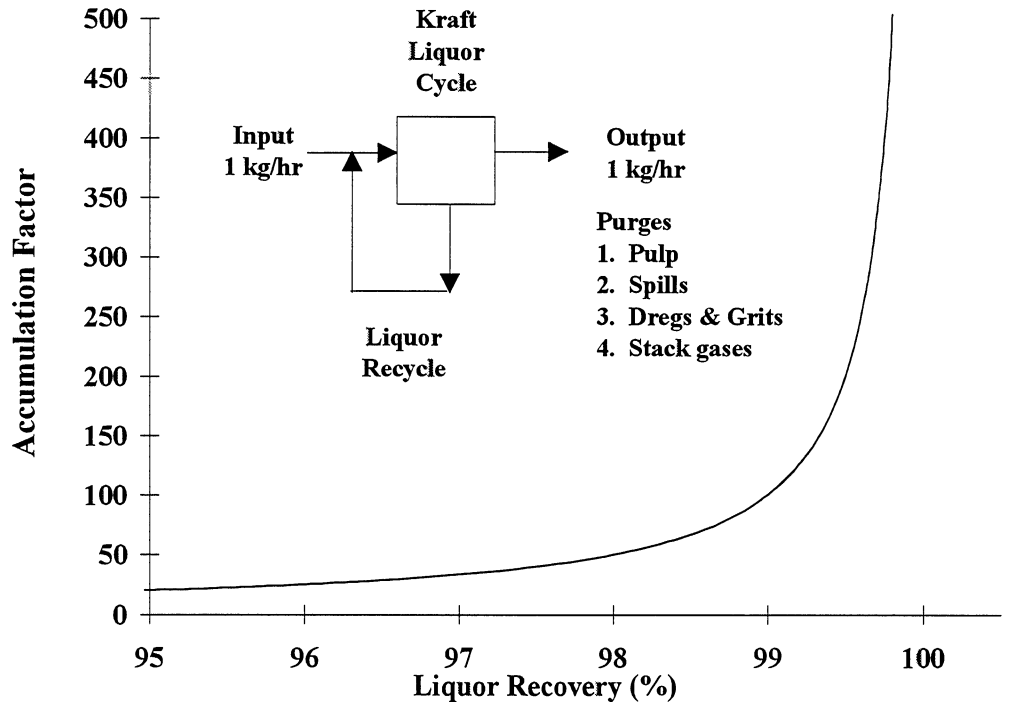

Figure 6. Mechanism of chloride and potassium build up in the kraft liquor cycle.

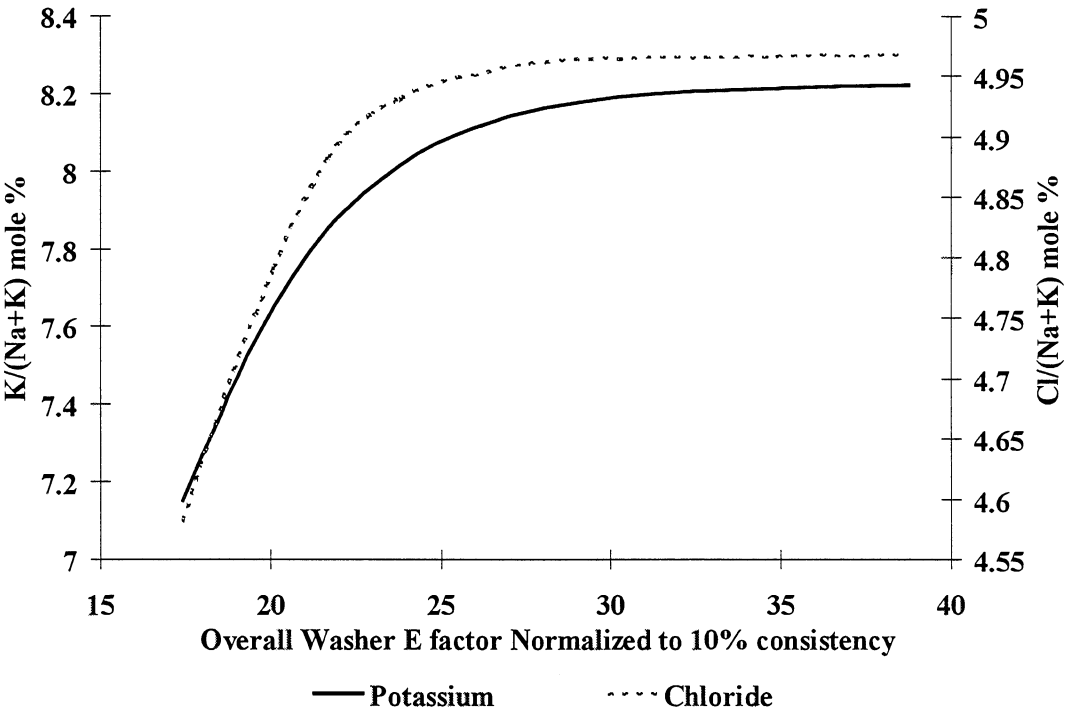

Figure 7. Simulated chloride and potassium concentrations in ESP dust as a function of overall brownstock washing Norden efficiency factor, E_{10}.

Figure 7 illustrates the increase of chloride and potassium concentrations in the kraft liquor cycle as the washing efficiency is improved and less chloride and potassium are purged with the pulp off the last washer(4). If a mill's current brownstock washing has an overall E_{10} factor (Norden efficiency factor normalized to washer discharge consistency of 10%) of less than 25 (without O_2 delignification), then improving washing efficiency to reduce washable solids carryover (COD) can have a noticeable impact on the chloride and potassium concentrations in the liquor cycle.

BLEACH PLANT COUNTER CURRENT WASHING

Reusing bleach plant filtrates in a counter current fashion back to the brownstock washers can change the metal profile throughout the fiberline. Recycling acidic bleach plant filtrates to the alkaline brownstock washers can create a "metal trap." The metal trap occurs because under acidic conditions most cations are desorbed from the pulp by ion exchange with hydrogen ions, and under alkaline conditions most of the cations are sorbed by the pulp by ion exchange with hydrogen ions. This sorption/desorption phenomenon between acid and alkaline wash stages results in a buildup of cations within the loop.

The concentration of cations in the filtrate must increase to the level where the amount being carried over with the pulp mat liquor in the bleach washer and the amount being carried back to recovery in the weak black liquor is equal to the amount entering the fiberline from the digester.

Counter current washing with bleach plant filtrates also results in an increase in dissolved solids throughout the fiberline. Increased sodium competition due to elevated sodium concentrations along with the effects carrying over dissolved organics into acidic bleach stages has actually resulted in a decrease of bound manganese to the Q-stage in several mill trials(3, 5-7).

PROCESS EQUIPMENT SCALING

Process equipment scaling in the fiberline can be a significant problem when bleach plant filtrates are recycled to the brownstock fiberline and the net bleach plant effluent discharges (purges) are reduced. Barium, calcium, and magnesium can form inorganic and organic deposits that plug fiberline process equipment.

Calcium carbonate and calcium oxalate are the two primary alkali-insoluble compounds of concern. Carbonate is formed in pulping reactions and enters as dead load with the white liquor. Oxalate is formed in pulping and bleaching reactions, particularly in oxidative bleaching stages such as oxygen and ozone.

Barium can form troublesome sulfate deposits in the bleach plant even under acidic conditions. Sulfate is often in relatively high concentrations in the bleach plant because sulfuric acid or spent acid from the ClO_2 generator are often used for pH control. Sulfate can also enter the bleach plant as carry-over from the brown stock fiberline.

Barium sulfate deposits have caused operation problems for many mills that recently converted to open ECF bleaching. The typical pH of 2.5-3.5 in ClO_2 delignification stages (D_0) is low enough to remove most of the barium from the pulp but not low enough to keep barium sulfate dissolved. The use of hydrochloric acid in the D_0 stage may be a solution for some mills running open bleach plants. Barium concentrations in the fiberline can be expected to increase as the bleach plant filtrates are closed back to the brownstock fiberline.

OXIDATIVE BLEACHING

In oxygen, ozone, and hydrogen peroxide bleaching, transition metals catalyze the decomposition of hydrogen peroxide that results in the formation of hydroxyl radicals. The hydroxyl radicals are nonselective and react with cellulose resulting in weaker fibers and lower yields.

The elements of most concern are Mn and Fe. Co and Cu are also catalytic, but are normally at very low levels (less than 1 ppm on dry fiber). Unlike other transition metals, Mn does not hurt the selectivity of oxidative bleaching reactions because hydroxyl radicals are not formed(8). Mg and Ca are important because they help counteract the effects of the transition metals by acting as stabilizers. A chelation wash is often preferred prior to a hydrogen peroxide bleach stage over an acid wash stage because it will remove transition metals with a maximum retention of the alkaline earth metals(9).

For efficient and selective ozone or hydrogen peroxide bleaching, a metal removal stage is required. A metal removal stage first desorbs the transition metals from the pulp and then removes them by washing out the filtrate containing the desorbed cations. The overall efficiency of the metal removal stage is a function of both the desorption and the washing. The desorption can be accomplished by either ion exchange or by chelation.

Iron

Control of iron is important for oxygen, ozone, and hydrogen peroxide bleaching because it catalyzes the rapid decomposition of peroxides resulting in the formation of nonselective hydroxyl radicals. The iron concentration on untreated kraft pulp is typically between 10-100 ppm on dry fiber. There are at least three forms of iron associated with pulp that make it difficult to characterize.

The first type of iron is a "nonequilibrium" suspended solid. This iron enters the fiberline as dirt with the chips. It can be controlled to some degree by chip washing. The dirt particles can appear small to the naked eye, but are very large relative to ionic dimensions. These particles have a relatively small surface area and are not in equilibrium with the cellulose binding sites. Under alkaline conditions the dissolution of the solid iron is limited by mass transfer and chemical kinetics. The dissolution rate of the solid iron increases with increasing temperature and decreasing pH. Once dissolved, the iron will behave as ionic iron and will be in equilibrium with the binding sites on the pulp.

An apparent increase in bound iron can appear after an acidic bleach stage without additional iron input. The average concentration of the solid iron is often not reflected in the analytical analysis of pulp because of errors associated with taking relatively small samples that may not have evenly distributed solid iron particles. Once dissolved in the acidic bleach stage, the iron is free to bind ionically to the pulp making it easier to detect when analyzing small samples(10).

The suspended solid type of iron is not evenly distributed on the pulp and often shows up as iron concentration spikes when analyzing multiple samples from the same pulp lot(10). Suspended solid iron also can confound a mill steady-state material balance by settling in filtrate tanks and then being swept out as tank levels drop creating transient increases in iron concentrations. Suspended solid iron is catalytically active, but because of its small surface area, it does not play a major role in the decomposition reactions of oxidative bleaching agents.

The second type of iron is ionic, either bound or in solution. Further studies are needed to adequately characterize the oxidation state of ionic iron in pulping and papermaking process streams. Ionic iron behaves as other ionic cations and competes for binding sites on pulp or other ligands and can be considered at equilibrium at most points in the fiberline. Ionic iron is highly catalytic and is the iron that must be controlled for oxidative bleach stages. Ionic iron can be removed using an acidic wash stage or by using a chelation wash stage.

The third type of iron is a tightly bound iron. It is unclear if this type of iron is bound ionically or covalently to fiber. This iron cannot be removed by acidic washing or chelation, but is removed with increasing delignification. The tightly bound iron is not catalytic and is of less concern than the ionic iron. When the tightly bound iron is removed by delignification, it becomes ionic in nature and is catalytically active.

PURGES

Conservation of mass requires that eventually the mass of NPEs entering the fiberline must leave the fiberline. In a fully closed-cycle fiberline, NPEs exit with the fiber product, with the weak black liquor, or with the aid of a metals removal process often referred to as an "artificial kidney." In a partially closed-cycle fiberline, NPEs may also exit with the sewered filtrate.

Filtrate Sewering

Filtrate sewering is the simplest method of controlling metals within the fiberline, but restricts the level of fiberline closure that can be achieved. The most desirable filtrate to sewer is an acid bleach stage's filtrate because the cations are not significantly bound to the pulp and most of the NPEs are acid soluble. The steady-state filtrate purge required can be determined by a combination of simulation and trial and error.

Metal Removal Process

Any process that can selectively remove NPEs from the filtrates of the fiberline is a candidate for a metals removal process or an "artificial kidney." There are a number of technologies to choose from, but the challenge has been to find a process that can be economically integrated into our current processes. The dissolved organics and pulp fines in most bleach plant filtrates modify NPE solubilities and tend to foul or plug many separation processes making an economical large-scale separation process technically challenging.

Natural Partitioning Manipulation

Ideally, the metal profile in the fiberline would be controlled by either purging metals from the digester with the weak black liquor (WBL) or purging them at the end of the bleach plant with the fiber. Forcing cations into the WBL at the digester would require an increase in the relative binding power of dissolved ligands compared to the fiber or by competition with other cations. This could be accomplished by either increasing the binding power of dissolved ligands (natural or added), by decreasing the affinity of fiber for the undesirable cations, or by displacing fiber bound cations with Na. Once the alkali-insoluble elements enter the liquor recovery cycle, they are purged from the system by dregs removal and the lime cycle purge.

Purging metals with the fiber and avoiding the "metal trap" would require either a completely alkaline fiberline or would require that the cations bind irreversibly to the fiber. Binding cations irreversibly to the fiber could have a significant impact on fiber bonding and final paper properties.

Manipulation of the natural partitioning of NPEs in the fiberline is not economically feasible today. However, current and future research in the industry may lead to economical methods of manipulating the natural partitioning of NPEs.

SUMMARY

Nonprocess element (NPE) concentrations within the fiberline increase as the degree of fiberline closure increases.

Potassium and chloride concentrations in the liquor cycle can increase with improved spill control and improved washing in the brownstock fiberline. Increased concentrations of potassium and chloride are undesirable because they can result in recovery boiler fouling and increased downtime.

Metal cation concentrations within the fiberline increase with increasing closure of acidic bleaching stages. Increased concentrations of calcium and barium can lead to scale deposits on process equipment. Increased concentrations of manganese and iron catalyze the decomposition of hydrogen peroxide leading to reduced bleaching efficiency and/or pulp strength loss in oxygen, ozone, and hydrogen peroxide stages.

Currently, fiberline metal concentrations can be controlled by using selective filtrate purges and/or metal removal processes.

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